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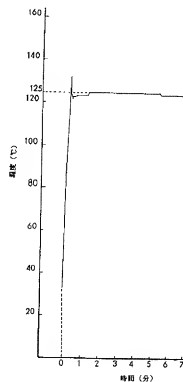
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(54) 【発明の名称】 多孔質膜及びその製造方法、並びにリチウムイオン2次電池

## (57) 【要約】

【課題】 ポリエチレンとポリプロピレンとを含む多孔質膜であって、ポリエチレンの溶融が起こると直ちに電流を遮断できる程度まで高抵抗化する多孔質膜を提供する。

【解決手段】 結晶化度70%のポリエチレンと結晶化度80%のポリプロピレンを用意し、これらを混合比(ポリプロピレン:ポリエチレン) 6:4の割合で混合した後フィルム化し、1軸延伸して、厚みが25 $\mu$ m、平均孔径が0.04 $\mu$ m、空孔率が45%の多孔質膜を作製する。この多孔質膜に電解液(LiBF<sub>4</sub> 溶解プロピレンカーボネート、DME 混合溶液)を含浸し、多孔質膜の両主面をステンレス製の電極で挟む。電極間に周波数100 kHzの正弦波交流電圧を実効値35Vで印加すると電圧印加開始後約2時間で最高温度(125℃)に達する。このような温度特性を示す多孔質膜はポリエチレンの溶融により急激に瞬時に高抵抗化する。



## 【特許請求の範囲】

【請求項1】 ポリエチレンとポリプロピレンを含んでなる多孔質膜であって、電解液を含浸させた多孔質膜の両主面に電極を配置し、この電極に交流電圧を印加して、多孔質膜を前記電解液の抵抗発熱によって10～50℃/秒の割合で昇温させた時の最高到達温度が（ポリエチレンの融点+20℃）以下であることを特徴とする多孔質膜。

【請求項2】 多孔質膜がポリエチレンとポリプロピレンの混合物の多孔質膜単体である請求項1に記載の多孔質膜。

【請求項3】 多孔質膜がポリエチレンとポリプロピレンの混合物からなる第1の多孔質膜とポリプロピレンからなる第2の多孔質膜を交互に積層した積層構造の多孔質膜である請求項1に記載の多孔質膜。

【請求項4】 請求項1に記載の多孔質膜を製造する方法であって、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンとを前記ポリエチレンの配合率が12重量%以上となるよう混合してなる膜状物を1軸延伸することにより多孔質化せしめる多孔質膜の製造方法。

【請求項5】 ポリエチレンの融点を $T_{m0}$ ℃とすると、膜状物を $-20^{\circ}\text{C} \sim (T_{m0}-30)^{\circ}\text{C}$ の低温度領域にて1軸延伸した後、 $(T_{m0}-30)^{\circ}\text{C} \sim (T_{m0}-2)^{\circ}\text{C}$ の高温温度領域にて前記低温度領域での延伸方向と同一または異なる方向に延伸して多孔質化せしめる請求項4に記載の多孔質膜の製造方法。

【請求項6】 低温度領域での延伸方向と高温温度領域での延伸方向とが同一方向であり、前記高温温度領域での延伸後に膜状物を前記低温度領域での延伸方向と異なる方向に再度延伸する請求項5に記載の多孔質膜の製造方法。

【請求項7】 膜状物全体当たりのポリエチレンの配合率の上限が90重量%である請求項4に記載の多孔質膜の製造方法。

【請求項8】 請求項1に記載の多孔質膜を製造する方法であって、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンとを混合してなる第1の膜状物と、ポリプロピレンからなる第2の膜状物とが交互に積層され、全体当たりのポリエチレンの配合率が12重量%以上にされた積層構造の膜状物を1軸延伸することにより多孔質化せしめる多孔質膜の製造方法。

【請求項9】 ポリエチレンの融点を $T_{m0}$ ℃とすると、積層構造の膜状物を $-20^{\circ}\text{C} \sim (T_{m0}-30)^{\circ}\text{C}$ の低温度領域で1軸延伸した後、 $(T_{m0}-30)^{\circ}\text{C} \sim (T_{m0}-2)^{\circ}\text{C}$ の高温温度領域にて前記低温度領域での延伸の延伸方向と同一または異なる方向に延伸して多孔質化せしめる請求項8に記載の多孔質膜の製造方法。

【請求項10】 低温度領域での延伸方向と高温温度領域

での延伸方向とが同一方向であり、前記高温温度領域での延伸後に積層構造の膜状物を前記低温度領域での延伸方向と異なる方向に再度延伸する請求項9に記載の多孔質膜の製造方法。

【請求項11】 積層構造の膜状物全体当たりのポリエチレンの配合率の上限が90重量%である請求項8に記載の多孔質膜の製造方法。

【請求項12】 請求項1に記載の多孔質膜に電解液を含浸させたものを一対の電極間に挟んでなるリチウムイオン2次電池。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】 本発明は多孔質膜及びその製造方法、並びにリチウムイオン2次電池（以下、略してリチウム2次電池とも称する。）に関する。

## 【0002】

【従来の技術】 種々のタイプの電池が実用に供されており、これら電池には正負両極間の短絡防止のために両極間にセパレータが介在せられる。

【0003】 近年、電子機器のコードレス化等に対応するための電池として、高エネルギー密度、高起電力、及び自己放電の少なさ等からリチウム2次電池が注目を浴びている。

【0004】 リチウム2次電池としては、例えば、負極材を金属リチウム、リチウムとアルミニウム等の金属との合金、カーボンやグラファイト等のリチウムイオンを吸着又は吸蔵する材料、またはリチウムイオンをドーピングした導電性高分子等で形成したもの知られている。また、正極材は、例えば一般に $(\text{C}_x\text{F}_y)_n$ で示されるフッ化黒鉛、 $\text{CoLiO}_2$ 、 $\text{MnO}_2$ 、 $\text{V}_2\text{O}_5$ 、 $\text{CuO}$ 、 $\text{Ag}_2\text{CrO}_4$ 等の金属酸化物、または $\text{TiO}_2$ 、 $\text{Cu}_2\text{S}$ 等の硫化物等で形成されている。

【0005】 このリチウム2次電池は、負極材としてのリチウムが強い反応性を有し、また、エチレンカーボネート、プロピレンカーボネート、アセトニトリル、γ-ブチラクトン、1,2-ジメトキシエタン、テトラヒドロフラン等の有機溶媒に $\text{LiPF}_6$ 、 $\text{LiCF}_3\text{SO}_3$ 、 $\text{LiClO}_4$ 、 $\text{LiBF}_4$ 等を電解質とした非水系の電解液を使用しているため、電池の誤使用によって外部短絡が生じると正極-負極間に電流が流れて、電解液の抵抗による発熱を生じて電池内部が著しく上昇し、遂には火災や破裂といった重大事故を引き起こす危険性がある。従って、このような事故を防ぐためにリチウム2次電池では安全対策のために種々の機構が施されている。例えば、電流遮断装置は、外部短絡により電池の温度が上昇した場合に電解液の蒸発などによって電池内部の気圧が上がるのを利用して、強制的に回路の一部を切断するよう構成されたものである。また、電池用セパレータが有するシャットダウン機構も安全機構の一つであり、これについては種々の提案がなされている。例えば、シ

3

ャットダウン開始設計温度に融点があるポリエチレンとポリエチレンより30℃程度融点が高いポリプロピレンの混合物（アロイ）の多孔質膜からなるもの（特開平4-206257）や、融点が異なる熱可塑性高分子の多孔質膜（具体的にはポリエチレンの多孔質膜とポリプロピレンの多孔質膜）を積層した積層多孔質膜からなるもの（特開平4-181651、特開昭62-10857）等がある。これらはいずれも多孔質膜の孔が溶融した樹脂によって塞がれて膜の電気抵抗（以下、単に抵抗と称する。）が増大することにより電流を遮断するものであり、低融点のポリエチレンが溶融することによりシャットダウンが低温で開始し、かつ、高融点のポリプロピレンがポリエチレンの溶融時に溶融せず、セパレータの膜形状を保持するよう働くことにより、充分な耐熱温度が得られるようになっている。なお、かかる多孔質膜からなるセパレータにおけるシャットダウン特性は、通常、電解液を含浸させたセパレータの両主面を電極で挟んでセルを形成し、このセルを乾燥機に投入した後、 $0.01 \sim 0.1^\circ\text{C}/\text{秒}$ 程度のなめらかな勾配でセルの温度を上昇させながら電極温度と電極間の抵抗値を測定し、この電極温度と抵抗値の関係から評価している。

#### 【0006】

【発明が解決しようとする課題】 昨今、リチウム2次電池の電池材料の改良が進み、電池の出力容量が大きくなっており、また、将来的にはなお一層の大容量化が進むことが予想される。例えば、正極材料であるCをNiに変更することで電池の出力容量は2～3割向上する。また、負極にコークス材を用いた場合、2倍近い出力容量を得ることも可能である（但し、負極材料以外の電池の構成要素の改良が必要）。しかしながら、電池の出力容量が大きくなると、外部短絡した時に正極と負極間に流れる電流値も大きくなり、外部短絡時の抵抗発熱（電解液の抵抗による発熱）による温度上昇も速くなる。従って、セパレータとしては、外部短絡した際に瞬時に電流を遮断できる程度に高抵抗化する優れた電流遮断特性（シャットダウン特性）を示すものが要求されるようになってきている。

【0007】 本発明は前記のような課題に鑑みてなされたものであり、ポリエチレンとポリプロピレンを含む多孔質膜であって、電池用セパレータとして使用した際にポリエチレンの溶融が起こると直ちに電流を遮断できる程度に高抵抗化する多孔質膜及びその製造方法を提供することを目的とする。

#### 【0008】

【課題を解決するための手段】 前記目的を達成するために、本発明者はポリエチレンとポリプロピレンからなる多孔質膜について鋭意検討し、以下の温度特性の得られる多孔質膜が優れた電流遮断特性を奏するものであることが判った。すなわち、本発明の多孔質膜は、ポリエチレンとポリプロピレンを含んでなる多孔質膜であっ

4

て、電解液を含浸させた多孔質膜の両主面に電極を配置し、この電極に交流電圧を印加して、多孔質膜を前記電解液の抵抗発熱によって $10 \sim 50^\circ\text{C}/\text{秒}$ の割合で昇温させた時の最高到達温度が（ポリエチレンの融点+ $20^\circ\text{C}$ ）以下であることを特徴としている。

【0009】 このような本発明の多孔質膜の温度特性は図1に示す評価試験機によって測定された。図1において、1は電解液が含浸されたポリエチレンとポリプロピレンからなる多孔質膜である。この電解液は一般のリチウム2次電池で使用されている電解液で、前記従来技術で説明した非水系のものである。1は電極、2は多孔質膜10の載置台を兼ねた電極であり、これらの電極は白金やステンレス網等のざねないもので形成されている。3は多孔質膜10を電極2の上面に固定するためのクリップ、4aは温度センサ、4は温度センサ4aで検知された温度を出力する温度計、5は交流電源である。電極1、2間に交流電源5により交流電圧を印加すると、電解液が含浸された多孔質膜10に電流が流れ、電解液の抵抗により発熱が生じて、多孔質膜10が温度上昇する。ここで、電源周波数は $1\text{kHz} \sim 10\text{MHz}$ 、電圧実効値は $5 \sim 200\text{V}$ の範囲で、電気抵抗による温度上昇率が $10 \sim 50^\circ\text{C}/\text{秒}$ （通電開始後2～5秒の平均）になるように調整されている。

【0010】 かかる通電状態を続けると多孔質膜10は温度上昇のためにポリエチレンが溶融する。多くの場合、このポリエチレンの溶融によって膜の抵抗が増大し、電流が流れなくなると温度上昇率が低下し、最高温度に到達した後、温度が徐々に低下する。ここで、最高到達温度が（ポリエチレンの融点+ $20^\circ\text{C}$ ）以下であるものは、ポリエチレンの溶融が始まると直ちに多孔質膜の電気抵抗が大きく増加して電流を有効に遮断したものであると解釈できる。このような温度特性を示す多孔質膜を電池にセパレータとして組み込んだ場合、外部短絡が生じると瞬時にシャットダウンが開始し、その後も膜形状が安定に維持されて優れたシャットダウン効果が得られる。一方、最高到達温度が（ポリエチレンの融点+ $20^\circ\text{C}$ ）より大きいものは、ポリエチレンの溶融が始まってから多孔質膜の抵抗が大きく増加するまでに時間がかり、この間に流れる電流によって膜の温度が（ポリエチレンの融点+ $20^\circ\text{C}$ ）より大きくなったものであると解釈できる。このような多孔質膜を電池にセパレータとして組み込んだ場合、外部短絡が生じた時のシャットダウンの開始は前記最高到達温度が（ポリエチレンの融点+ $20^\circ\text{C}$ ）以下である膜を用いた場合のそれに比して大きく遅れ、また、膜形状を安定に維持することができず、優れたシャットダウン効果が得られなかった。また、前記とは異なり、通電開始後、多孔質膜の温度が上昇し続け、最高到達温度を示す前に、ポリプロピレンが溶融してピンホールを発生してしまうものもあった。なお、従来の乾燥機に投入する方法では、単に温度とイン

ピーダンスの関係を見ていた。これに対し、上記記載の本発明の方法では、インピーダンスを測定するような微小電流を流しただけでは予測できない、膜に孔が開くという現象も確認でき、これがまさに電池の安全性に重要となる。

【0011】また、本発明の第1の多孔質膜の製造方法は、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンとを前記ポリエチレンの配合率が12重量%以上となるよう混合してなる膜状物を1軸延伸することにより多孔質化せしめる。かかる製造方法によれば、前記温度特性を有する本発明の多孔質膜、すなわち、ポリエチレンの電融が始まるのと直ちに電流を遮断できる程度までの電気抵抗が増大する多孔質膜を合理的に製造することができる。

【0012】また、本発明の第2の多孔質膜の製造方法は、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンとを混合してなる第1の膜状物と、ポリプロピレンからなる第2の膜状物とが交互に積層され、全体当たりのポリエチレンの配合率が12重量%以上にされた積層構造の膜状物を1軸延伸することにより多孔質化せしめる。かかる製造方法によれば、前記第1の製造方法と同様に前記温度特性を有する本発明の多孔質膜を合理的に製造することができる。と、得られる多孔質膜はポリプロピレンの多孔質膜を含む積層構造になり、ポリエチレン溶融時に膜形状がより安定に維持される多孔質膜を得ることができる。

【0013】また、本発明のリチウムイオン2次電池は、前記温度特性を有する本発明の多孔質膜に電解液を含浸させたものを一対の電極間に挟んで構成したものである。このような構成にしたことにより、外部短絡しても発火やショートが起らず、安定動作するリチウムイオン2次電池にできる。

【0014】

【発明の実施の形態】本発明の多孔質膜は前記した温度特性を有するものであって、その製造方法は特に限定されないが、以下に環境汚染の心配がなく、工程（作業）が簡単な製造方法の一例を説明する。これは、この種の分野で従来から行われている多孔質膜の製法、すなわち、ポリエチレンとポリプロピレンの混合物（アロイ）の膜状物を得、この膜状物を延伸することによって多孔質化せしめる方法において、ポリエチレンとして結晶化度が60%より大きいもの（好ましくは70%以上のもの）、ポリプロピレンとして結晶化度が70%より大きいもの（好ましくは80%以上のもの）を用いる方法である。なお、従来は一般に結晶化度が40～60%のポリエチレンと結晶化度が50～70%のポリプロピレンが用いられている。前記結晶化度は示差走査熱量計（DSC）により測定した値である。

【0015】かかる製法によって得られる多孔質膜が前記した温度特性を有するものとなる理由は明らかではな

いが、本発明者は次のように推察している。すなわち、同じ条件で延伸したとしても、結晶化度の高い材料は延伸されやすく、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンの膜状物を延伸した場合、従来の結晶化度が40～60%のポリエチレンと結晶化度が50～70%のポリプロピレンの膜状物を延伸した場合よりも、ポリエチレン及びポリプロピレンの双方とも大きく引き延ばされることとなる（特に、ポリエチレンが大きく引き延ばされる。）。従って、本発明の結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポリプロピレンの膜状物を延伸して得られる多孔質膜は、図2（a）に示すように、平たく引き延ばされた形状のポリエチレン部10aがポリプロピレン部10bで囲まれた状態になる。一方、従来の結晶化度が40～60%のポリエチレンと結晶化度が50～70%のポリプロピレンの膜状物を延伸して得られる多孔質膜は、図2（b）に示すように、実質的に球形のポリエチレン部10aがポリプロピレン部10bで囲まれた状態になる。なお、図では孔を省略しているが、ポリエチレン部10a及びポリプロピレン部10bの双方に孔が形成されている。これら双方の多孔質膜のいずれにおいても、温度上昇によりポリエチレンが溶融してポリエチレン部10aの孔が塞がると、ポリエチレン部10aには電流は流れず、ポリプロピレン部10bを縫うように電流が流れることになるが、図2

（a）の本発明の多孔質膜ではポリプロピレン部10bを流れる電流11の電流経路が長く、図2（b）の従来の多孔質膜ではポリプロピレン部10bを流れる電流12の電流経路が短くなる。従って、図2（a）の本発明の多孔質膜では、ポリエチレンが溶融してポリエチレン部10aの孔が塞がった時点で膜全体の抵抗が大きく増加し、電流遮断効果（シャットダウン効果）が得られ、膜の温度が一旦上昇し、最高温度が（ポリエチレンの融点+20℃）を越えない範囲で低下することとなる。一方、図2（b）の従来の多孔質膜では、ポリエチレンが溶融してポリエチレン部10aの孔が塞がれても、ポリエチレン部10aの孔が塞がれる前（ポリエチレン部10aとポリプロピレン部10bの両方にある孔を介して電流が流れる状態）と電流経路の長さは殆ど変わらないため、この時点での膜全体の抵抗の増加は小さく、この後溶融したポリエチレンがポリプロピレン部10bの孔を塞いだ時点で、膜全体の抵抗が大きく増加し、電流遮断効果（シャットダウン効果）が得られ、その結果、膜の温度が（ポリエチレンの融点+20℃）を越える温度まで上昇した後低下することとなる。

【0016】前記において、ポリエチレンとポリプロピレンの混合物（アロイ）の膜状化（フィルム化）は、例えばTダイ押出法、インフレーション法等の公知の方法で行われる。また、ポリエチレンとポリプロピレンのアロイの膜状物を延伸する方法としては、ロール延伸、テ

ンター延伸等の方法で1軸方向に延伸する方法(第1方法)、低温度領域で1軸延伸した後、この延伸の延伸方向と同一の延伸方向に高温度領域で再度延伸する方法

(第2方法)、低温度領域で1軸延伸した後、この延伸の延伸方向とは延伸方向を変えて高温度領域にて再度延伸する方法(第3方法)、低温度領域で1軸延伸した後、この延伸の延伸方向と同一の延伸方向に高温度領域にて再度延伸し、更にこの延伸と延伸方向を換えて再度延伸を行う方法(第4方法)等が採用される。1回の延伸を行う第1の方法ではポリエチレンの融点を $T_{ab}$ ℃とすると、 $-20^{\circ}\text{C} \sim (T_{ab}-2)^{\circ}\text{C}$ の温度領域で行うのが好ましい。また、2回以上の延伸を行う第2～第4方法での低温度領域及び高温度領域は、ポリエチレンの融点を $T_{ab}$ ℃とすると、低温度領域が $-20^{\circ}\text{C} \sim (T_{ab}-30)^{\circ}\text{C}$ の温度領域であり、高温度領域が $(T_{ab}-30)^{\circ}\text{C} \sim (T_{ab}-2)^{\circ}\text{C}$ の温度領域であるのが好ましい。これは、これらの温度領域でそれぞれの延伸を行うこと、膜状物を効率良く延伸され、しかも孔径の拡大が充分になされて、後述する好ましい孔径(0.005～1 $\mu\text{m}$ )、空孔率(20～80%)を有する多孔質膜を再現性よく得ることができるためである。また、第4方法で延伸した場合、第1～第3方法よりも、孔径の拡大及び膜内に孔を一樣に存在させる点においてより好ましい結果をもたらす。これらの延伸方法による延伸を行った際の膜状物の延伸倍率は、すなわち、下記式(数1)で表される延伸倍率は一般に5～600%、好ましくは20～300%である。式(数1)中、 $L_0$ は延伸前の膜状物の長さ、 $L_1$ は延伸後の最終的な膜状物の長さである。

【0017】

【数1】

$$\text{延伸倍率}(\%) = \frac{L_1 - L_0}{L_0} \times 100$$

【0018】また、1回の延伸工程からなる第1方法においても、複数回の延伸工程からなる第2～第4方法においても、各工程での延伸速度は、一般に10～5000%/min、好ましくは100～10000%/minである。

【0019】前記ではポリエチレンとポリプロピレンのアロイの多孔質膜一層からなる多孔質膜について説明したが、従来から提案されているポリエチレンとポリプロピレンのアロイの多孔質膜(アロイ層)とポリプロピレンの多孔質膜(ポリプロピレン層)とを積層したタイプの多孔質膜においても、ポリエチレンとポリプロピレンのアロイ層を得る際に、結晶化度が60%より大きいポリエチレンと、結晶化度が70%より大きいポリプロピレンを用いることにより、本発明の被加熱温度特性を有する多孔質膜にできる。すなわち、結晶化度が60%より大きいポリエチレンと結晶化度が70%より大きいポ

リプロピレンのアロイの膜状物と、ポリプロピレンの膜状物を積層し、これを前記と同様の延伸方法で延伸して多孔質化する。ここでの積層構造はアロイ層とポリプロピレン層の2層構造、アロイ層の両主面にポリプロピレン層を重ねた3層構造、ポリプロピレン層の両主面にアロイ層を重ねた3層構造、アロイ層とポリプロピレン層の交互にトータルの層数が4層以上となるよう積層した多層構造のいずれであってもよい。

【0020】また、ポリエチレンとポリプロピレンのアロイの多孔質膜一層からなる多孔質膜を得る場合であっても、ポリエチレンとポリプロピレンのアロイの多孔質膜(アロイ層)とポリプロピレンの多孔質膜(ポリプロピレン層)とを積層したタイプの多孔質膜を得る場合であっても、膜状物を延伸する前に膜状物にアニーリングを施すことができる。このアニーリングは多孔質化時に空孔率を高める働きをする。このアニーリングは $(T_{ab}-30)^{\circ}\text{C} \sim (T_{ab}-2)^{\circ}\text{C}$ の温度領域で行うのが好ましく、数秒～数時間程度行われる。

【0021】以上の製造方法によって本発明の多孔質膜を製造する場合、膜全体に対するポリエチレンの配合率が12重量%以上としなければならぬことを実験により確認している。これは、恐らく、ポリエチレンの配合率が12重量%に満たない場合は、膜中に平たく引き延ばされた形状で存在するポリエチレン部の存在量が小さくなり過ぎ、電流経路を長大化が充分になさなくなるためであると考えられる。また、膜全体に対するポリエチレンの配合率が90重量%を超える場合は、ポリエチレンが溶融した時に膜形状を維持できなくなる場合があり、膜全体に対するポリエチレンの配合率の上限は90重量%にするのが好ましい。

【0022】本発明の多孔質膜の孔径は一般に0.005～1 $\mu\text{m}$ 、好ましくは0.01～0.5 $\mu\text{m}$ である。空孔率は一般に20～80%、好ましくは30～70%である。また、本発明の多孔質膜を構成するポリエチレンの種類は特に限定されるものではなく、低密度、中密度、または高密度のポリエチレンや、直鎖状のポリエチレン等の各種ポリエチレンを用いることができる。また、ポリプロピレンの種類も特に限定されるわけではないが、高い空孔率を得るためにはアイソタクチックインデックスが90%以上、好ましくは95%以上のアイソタクチックポリプロピレンを用いるのが好ましい。

【0023】本発明の多孔質膜はリチウム2次電池のセパレータだけでなく、もちろん、リチウム(イオン)1次電池や他のタイプ電池のセパレータとしても使用できる。

【0024】

【実施例】

(実施例1) 結晶化度70%のポリエチレンと、結晶化度80%のポリプロピレンを用意し、これらを混合比(ポリエチレン:ポリプロピレン)6:4の割合で混合

した後フィルム化し、熱を加え(115℃で)延伸倍率160%の1軸延伸を行って、厚みが25 $\mu$ m、平均孔径が0.04 $\mu$ m、空孔率が45%の多孔質膜を作製した。そして、この多孔質膜に電解液(LiBF<sub>4</sub> 溶融プロピレンカーボネートとDMF(ジメチルセキタン)の混合溶液)を含浸し、両主面をステンレス製の電極で挟んだ。そして、この両主面が電極で挟まれた多孔質膜を前記図1に示した評価試験機に搭載し、周波数100kHzの正弦波交流電圧を実効値3Vで印加した。この時の温度上昇率(通電開始後2~5秒の平均)は20℃/秒であった。図3は正弦波交流電圧印加開始後の多孔質膜の温度変化特性を示した図であり、電圧印加開始後約2分で最高到達温度に達し、約5.5分を経過した後温度が低下した。最高到達温度は125℃で、これは(ポリエチレンの融点(125℃+20℃)である145℃以下であった。そして、この多孔質膜をリチウムイオン2次電池に組み込み、過充電状態(過充電後1Cで1時間充電して200%の充電状態)にして、外部短絡試験を行った。ここで、このリチウムイオン2次電池は、アルミ箔に活物質としてのLiCoO<sub>2</sub>と導電助材としてのカーボンとN-メチルピロリドン(NMP)の混合物を塗布し乾燥して得られた正極材と電解液に活物質としての黒鉛とNMPの混合物を塗布し乾燥して得られた負極材との間に前記多孔質膜にエチレンカーボネート(EC)とDMC(ジメチルカーボネート)を等量(体積比1:1)混合した溶液1リットルにLiPF<sub>6</sub>を1モル溶解した電解液を含浸させたものを挟んでなる積層体をセクタンの周りに複数重ねて巻き付け、この巻回物を負極缶に収容し、正極蓋で封止してなる単三電池である(負極缶には安全弁が設けられている。)。外部短絡試験の結果、電池はショートや発火は全く起こらず安定に動作し、電池管壁温度も100℃以下であった。なお、前記1Cの[C]は、電池の充放電電流の大きさを表す単位であり、1Cは電池を1時間で完全放電状態から満充電状態(満充電状態から完全放電状態)にする電流値を示す(例えば、750mAの電池では1Cは750mA、2Cは750 $\times$ 2=1500mA、0.5Cは750/2=375mAとなる)。

【0025】(比較例1)結晶化度50%のポリエチレンと、結晶化度60%のポリプロピレンを用いた以外は、前記実施例1と同様に多孔質膜を得た。そして、この多孔質膜について前記実施例1と同様の試験を行った。図4はこの時の正弦波交流電圧印加開始後の多孔質膜の温度変化特性を示した図であり、電圧印加開始後約2秒で150℃まで達した。最高到達温度は更に高いと予想できるが、電圧印加を続けて行くと多孔質膜が溶融して正極-負極間がショートしたため、電源の安全装置が働いて通電が停止し、これ以上の測定が不可能となった。そして、この多孔質膜を前記実施例1と同様にして電池に組み込み、過充電後の外部短絡試験を行っ

たところ、電池10個のうち2個が電池管壁温度が120℃以上に上昇した。

【0026】(実施例2)結晶化度70%のポリエチレンと結晶化度80%のポリプロピレンを用意し、これらを混合比(ポリエチレン:ポリプロピレン)5:5の割合で混合した後膜状化(フィルム化)して第1の膜状物(フィルム)を得た。また、ポリプロピレン単体からなる第2の膜状物(フィルム)を別に作製した。そして、第1の膜状物(フィルム)の両主面にそれぞれ第2の膜状物を重ね、この積層物を熱を加え(115℃で)延伸倍率160%の1軸延伸を行って、厚みが25 $\mu$ mの積層多孔質膜を作製した。3層の厚さの比率は1:1:1であり、膜全体当たりのポリエチレンの配合率は16.7重量%であった。そして、この積層多孔質膜について前記実施例1と同様の試験を行った。図5はこの時の正弦波交流電圧印加開始後の多孔質膜の温度変化特性を示した図であり、電圧印加開始後約11分で最高到達温度に達した。最高到達温度は127℃で、これは(ポリエチレンの融点(125℃+20℃)である145℃以下であった。続いて、前記実施例1と同様にこの多孔質膜をリチウムイオン2次電池に組み込み、外部短絡試験を行ったところ、ショートや発火は全く起こらず安定に動作し、電池管壁温度も100℃以下であった。

【0027】(比較例2)第1の膜状物(フィルム)の原料として結晶化度が50%のポリエチレンと、結晶化度が60%のポリプロピレンを用いた以外は、前記実施例2と同様に三層構造の積層構造の積層多孔質膜を得た。そして、この多孔質膜について前記実施例1と同様の試験を行った。図6はこの時の正弦波交流電圧印加開始後の多孔質膜の温度変化特性を示した図であり、最高到達温度は157℃で、これは(ポリエチレンの融点(125℃+20℃)である145℃より高くなった。前記実施例1と同様に、この多孔質膜をリチウムイオン2次電池に組み込み、外部短絡試験を行ったところ、電池10個のうち2個が電池管壁温度が120℃以上に上昇した。

【0028】(比較例3)3層の厚さの比率を2:1:1(真ん中の第1の膜状物が多孔質化されて得られた層の厚みを小さく、両方の第2の膜状物が多孔質化されて得られた層の厚みを大きく)にし、膜全体当たりのポリエチレンの含有率が10重量%に以上以外は前記実施例2と同様に三層構造の積層構造の積層多孔質膜を得た。図7はこの時の正弦波交流電圧印加開始後の多孔質膜の温度変化特性を示した図であり、最高到達温度は160℃で、(ポリエチレンの融点(125℃+20℃)である145℃より高かった。続いて、前記実施例1と同様に、この多孔質膜をリチウムイオン2次電池に組み込み、外部短絡試験を行ったところ、電池10個のうち2個が電池管壁温度が120℃以上に上昇した。

【0029】

11

【発明の効果】以上のように、本発明によれば、ポリエチレンとポリプロピレンからなる多孔質膜であって、電池用セパレータとして使用した場合に優れた電流遮断効果（シャットダウン効果）、すなわち、ポリエチレンの溶融後、瞬時に電流を遮断できる程度まで高抵抗化してシャットダウンする多孔質膜を提供することができる。また、かかる本発明の多孔質膜を簡単かつ合理的に製造できる多孔質膜の製造方法を提供することができる。また、外部短絡しても発火やショートが起こらず、安定動作するリチウムイオン二次電池を提供することができる。

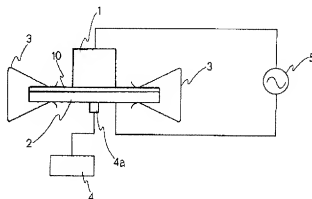
【図面の簡単な説明】

【図 1】 多孔質膜の温度特性は評価する評価試験機の概略構成を示した側面図である。

【図 2】 本発明と従来のポリエチレンとポリプロピレンのアロイの多孔質膜の膜構造を模式的に示した断面斜視図である。

【図 3】 実施例 1 による多孔質膜の正弦波交流電圧印加開始後の多孔質膜の温度変化を示した図である。

【図 1】



12

【図 4】 比較例 1 による多孔質膜の正弦波交流電圧印加開始後の多孔質膜の温度変化を示した図である。

【図 5】 実施例 2 による多孔質膜の正弦波交流電圧印加開始後の多孔質膜の温度変化を示した図である。

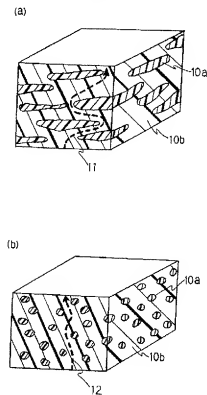
【図 6】 比較例 2 による多孔質膜の正弦波交流電圧印加開始後の多孔質膜の温度変化を示した図である。

【図 7】 比較例 3 による多孔質膜の正弦波交流電圧印加開始後の多孔質膜の温度変化を示した図である。

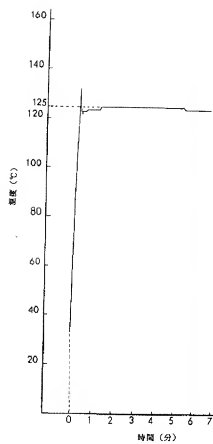
【符号の説明】

- 10 1 電極  
2 多孔質膜の載置台を兼ねた電極  
3 多孔質膜を電極の上面に固定するためのクリップ  
4 a 温度センサ  
4 温度センサで検知された温度を出力する温度計  
5 交流電源  
10 電解液が含まれた多孔質膜  
10 a ポリエチレン部  
10 b ポリプロピレン部  
11, 12 電流

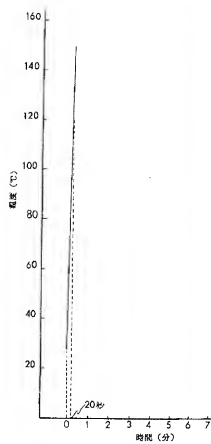
【図 2】



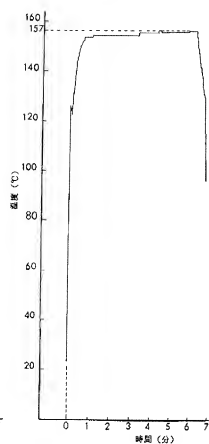
【図3】



【図4】

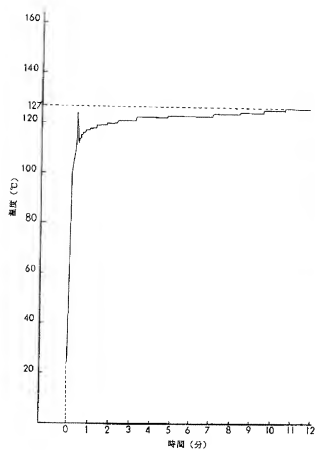


【図6】

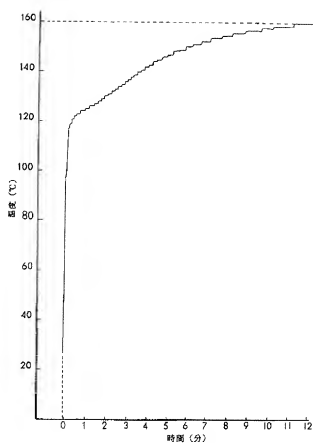




【図5】



【図7】



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(21)Application number : 08-056392 (71)Applicant : NITTO DENKO CORP

(22)Date of filing : 13.03.1996 (72)Inventor : SAEN HAJIME

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(54) POROUS MEMBRANE, ITS PRODUCTION, AND LITHIUM ION  
SECONDARY CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a porous membrane which contains polyethylene and polypropylene, and is useful in the production of lithium ion secondary cells because it has specific temperature characteristics, shows excellent current-breaking properties as a battery separator, when used as a cell separator and stably works without ignition of fire by the external short-circuit.

SOLUTION: This membrane is porous membrane containing (A) polyethylene and (B) polypropylene (for example, a simple porous membrane of a mixture of A and B or a porous membrane formed by alternately laminating a porous membrane of an A and B mixture and a porous membrane of B). When the porous membrane is impregnated with an electrolyte solution, electrodes are arranged onto both main faces of the porous membrane and an alternating voltage is applied to the electrodes to raise the temperature of the membrane at

a rate of 10-50°C/second by the resistance heat of the electrolyte solution, the maximum temperature to be reached is adjusted to be equal to or less than (the melting point of the component A +20°C). This porous membrane is prepared, for example, by mixing component A of  $\geq 60\%$  crystallinity with component B of  $\leq 70\%$  crystallinity so that the proportion of component A becomes  $\geq 12\text{wt.}\%$  and by monoaxially orienting the membrane of the mixture.

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[Date of extinction of right]

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

[Claim 1] Porous membrane characterized by being the porous membrane which comes to contain polyethylene and polypropylene, and the highest attainment temperature when having arranged the electrode to both the principal planes of porous membrane into which the electrolytic solution was infiltrated, impressing alternating voltage to this electrode, and carrying out the temperature up of the porous membrane at a rate of 10-50 degrees C/second by resistance generation of heat of said electrolytic solution being the following (melting point of +20 degrees C of polyethylene).

[Claim 2] Porous membrane according to claim 1 whose porous membrane is

the porous membrane simple substance of the mixture of polyethylene and polypropylene.

[Claim 3] Porous membrane according to claim 1 which is the porous membrane of the laminated structure which carried out the laminating of the 1st porous membrane which porous membrane turns into from the mixture of polyethylene and polypropylene, and the 2nd porous membrane which consists of polypropylene by turns.

[Claim 4] The manufacture approach of the porous membrane made to porosity-ize by extending one shaft of filmy materials which mixed and become so that it may be the approach of manufacturing porous membrane according to claim 1 and the rate of combination of said polyethylene may become 12 % of the weight or more about polyethylene with larger crystallinity than 60%, and polypropylene with larger crystallinity than 70%.

[Claim 5] The manufacture approach of the porous membrane according to claim 4 extends in the same as that of the extension direction in a field, or the different direction, and it is made to porosity-ize whenever [ said low-temperature ] in the high temperature field of  $T_{mb}-30$  -  $(T_{mb}-2)$  after extending one shaft of filmy materials in a field whenever [ low-temperature / of  $-20$  degrees C -  $(T_{mb}-30)$  ], if the melting point of polyethylene is made into  $T_{mb}$  degree C.

[Claim 6] The manufacture approach of the porous membrane according to claim 5 which the extension direction in a field and the extension direction in a high temperature field are the same directions whenever [ low-temperature ], and extends a filmy material again in the extension direction in a field, and the different direction whenever [ said low-temperature ] after extending in said high temperature field.

[Claim 7] The manufacture approach of porous membrane according to claim 4 that the upper limit of the rate of combination of the polyethylene per whole filmy material is 90 % of the weight.

[Claim 8] The manufacture approach of the porous membrane made to porosity-ize by extending one shaft of filmy materials of a laminated structure with which it is the approach of manufacturing porous membrane according to claim 1, the laminating of the 1st filmy material which comes to mix polyethylene with larger crystallinity than 60% and polypropylene with larger crystallinity than 70%, and the 2nd filmy material which consists of polypropylene was carried out by turns, and it \*\*\*\*ed the rate of combination of the polyethylene per whole to 12% of the weight or more.

[Claim 9] The manufacture approach of the porous membrane according to claim 8 extends in the same as that of the extension direction of extension in a field, or the different direction, and it is made to porosity-ize whenever [ said

low-temperature ] in the high temperature field of \*\* (Tmb-30) - (Tmb-2) \*\* after extending one shaft of filmy materials of a laminated structure in a field whenever [ low-temperature / of -20 degrees C - (Tmb-30) \*\* ], if the melting point of polyethylene is made into Tmbdegree C.

[Claim 10] The manufacture approach of the porous membrane according to claim 9 which the extension direction in a field and the extension direction in a high temperature field are the same directions whenever [ low-temperature ], and extends the filmy material of a laminated structure again in the extension direction in a field, and the different direction whenever [ said low-temperature ] after extending in said high temperature field.

[Claim 11] The manufacture approach of porous membrane according to claim 8 that the upper limit of the rate of combination of the polyethylene per whole filmy material of a laminated structure is 90 % of the weight.

[Claim 12] The lithium ion rechargeable battery which comes to insert into inter-electrode [ of a pair ] what infiltrated the electrolytic solution into porous membrane according to claim 1.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to porous membrane and its manufacture approach, and a list at a lithium ion rechargeable battery (hereafter, it omits and is also called a lithium rechargeable battery.).

[0002]

[Description of the Prior Art] Practical use is presented with the cell of various types, and a separator is made to intervene among two poles for the short circuit prevention between positive/negative two poles by these cells.

[0003] The lithium rechargeable battery is capturing the spotlight from a high energy consistency, high electromotive force, the little of self-discharge, etc. as a cell for corresponding to cordless-ization of electronic equipment etc. in recent years.

[0004] As a lithium rechargeable battery, what formed adsorption, the ingredient which carries out occlusion, or the lithium ion by the doped conductive polymer is known [ lithium ions /, such as an alloy of a metal lithium, a lithium, and metals, such as aluminum, carbon, and graphite, ] in negative-electrode material, for example. Moreover, positive-electrode material is formed with sulfides, such as a metallic oxide of graphite fluoride [ which is shown by n generally (CF<sub>x</sub>) ], CoLiO<sub>2</sub>, MnO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, CuO, and Ag<sub>2</sub>CrO<sub>4</sub> grade or TiO<sub>2</sub>, and CuS, etc.

[0005] This lithium rechargeable battery has reactivity with the strong lithium as negative-electrode material. Moreover, ethylene carbonate, propylene carbonate, an acetonitrile, organic solvents, such as gamma-butyrolactone, 1, 2-dimethoxyethane, and a tetrahydrofuran, -- LiPF<sub>6</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiClO<sub>4</sub>, and LiBF<sub>4</sub> etc., since the electrolytic solution of the non-drainage system used as the electrolyte is used. If an external short circuit arises by misuse of a cell, a current will flow between positive-electrode-negative electrodes, generation of heat by resistance of the electrolytic solution is produced, the interior of a cell goes up remarkably and there is a danger of causing major accidents, such as \*\*\*\*\* and a burst, at last. Therefore, in order to prevent such accident, in the lithium rechargeable battery, various devices are given for the safety practice. For example, when the temperature of a cell rises by the external short circuit, a current interrupting device is constituted so that evaporation of the electrolytic solution etc. may cut a part of circuit compulsorily using the atmospheric pressure inside a cell going up. Moreover, the shutdown device which the separator for cells has is also one of the insurance devices, and various proposals are made about this. For example, there are what about 30 degrees C of melting points become from the porous membrane of the mixture (alloy) of high polypropylene from the polyethylene which has the melting point in a shutdown initiation design temperature, and polyethylene (JP,4-206257,A), a

thing (JP,4-181651,A, JP,62-10857,A) which consists of laminating porous membrane which carried out the laminating of the porous membrane (they are specifically the porous membrane of polyethylene and the porous membrane of polypropylene) of the thermoplastic giant molecule with which the melting points differ. when each of these be close by the resin which the hole of porous membrane fused , a membranous electric resistance ( resistance be only call hereafter . ) increase , and a current be intercept , a shutdown begin at low temperature when the polyethylene of a low-melt point point fuse , and it work [ high-melting polypropylene do not fuse at the time of melting of polyethylene , but ] so that the film configuration of a separator may be hold , sufficient heat-resistant temperature be acquire . In addition, after the shutdown property in the separator which consists of this porous membrane usually forms a cel on both sides of both the principal planes of a separator into which the electrolytic solution was infiltrated with an electrode and supplies this cel to a dryer, it measures electrode temperature and inter-electrode resistance, raising the temperature of a cel with about 0.01-0.1 degrees C [/second ] smooth inclination, and is evaluating them from this electrode temperature and the relation of resistance.

[0006]

[Problem(s) to be Solved by the Invention] It is expected that amelioration of the

cell ingredient of a lithium rechargeable battery progresses, and the output capacitance of a cell is large, and prospective in addition much more large capacity-ization progresses these days. For example, the output capacitance of a cell improves 2 to 30 percent by changing into nickel Co which is a positive-electrode ingredient. Moreover, when corks material is used for a negative electrode, it is also possible to obtain a twice [ about ] as many output capacitance as this (however, amelioration of the component of cells other than a negative-electrode ingredient need). However, if the output capacitance of a cell becomes large, when an external short circuit is carried out, the current value which flows between a positive electrode and a negative electrode will also become large, and the temperature rise by resistance generation of heat at the time of an external short circuit (generation of heat by resistance of the electrolytic solution) will also become quick. Therefore, as a separator, when an external short circuit is carried out, what shows the outstanding current barrier property (shutdown property) formed into high resistance to extent which can intercept a current in an instant is required increasingly.

[0007] This invention is made in view of the above technical problems, it is the porous membrane containing polyethylene and polypropylene, and if melting of polyethylene happens when it is used as a separator for cells, it will aim at offering the porous membrane formed into high resistance, and its manufacture

approach to extent which can intercept a current immediately.

[0008]

[Means for Solving the Problem] In order to attain said purpose, this invention persons examined wholeheartedly the porous membrane which consists of polyethylene and polypropylene, and it turned out that it is what does so the current barrier property excellent in the porous membrane from which the following temperature characteristics are acquired. That is, the porous membrane of this invention is porous membrane which comes to contain polyethylene and polypropylene, it arranges an electrode to both the principal planes of porous membrane into which the electrolytic solution was infiltrated, impresses alternating voltage to this electrode, and is characterized by the highest attainment temperature when carrying out the temperature up of the porous membrane at a rate of 10-50 degrees C/second by resistance generation of heat of said electrolytic solution being the following (melting point of +20 degrees C of polyethylene).

[0009] The temperature characteristic of the porous membrane of such this invention was measured by the evaluation testing machine shown in drawing 1 . In drawing 1 , 10 is porous membrane which the electrolytic solution becomes from the polyethylene with which it sank in, and polypropylene. This electrolytic solution is the electrolytic solution currently used by the general lithium

rechargeable battery, and is the thing of a non-drainage system explained with said conventional technique. It is the electrode with which 1 served as the electrode and 2 served as the installation base of porous membrane 10, and neither platinum nor a stainless steel rope rusts, and these electrodes are formed. The thermometer which outputs the temperature as which a clip for 3 to fix porous membrane 10 to the top face of an electrode 2 and 4a were detected with the temperature sensor, and 4 was detected by temperature sensor 4a, and 5 are AC power supply. If alternating voltage is impressed by AC power supply 5 between an electrode 1 and 2, a current will flow to the porous membrane 10 into which the electrolytic solution sank, generation of heat will arise by resistance of the electrolytic solution, and porous membrane 10 will carry out a temperature rise. Here, a power line period is 1kHz - 10MHz, and the range of electrical-potential-difference actual value is 5-200V, and it is adjusted so that the rate of a temperature rise by electric resistance may become [ second ] in 10-50 degrees C (average which is after [ energization initiation ] 2 - 5 seconds) /. [0010] If this energization condition is continued, polyethylene will fuse porous membrane 10 for a temperature rise. After in many cases membranous resistance increasing, a current's not flowing, and the rate of a temperature rise falling and reaching a maximum temperature by melting of this polyethylene, temperature falls gradually. Here, that whose highest attainment temperature is

the following (melting point of +20 degrees C of polyethylene) can be interpreted as the electric resistance of porous membrane increasing greatly and intercepting a current effectively immediately, if melting of polyethylene starts. the porous membrane which shows such the temperature characteristic is constructed as a separator on a cell, and it is \*\* -- a case -- an external short circuit -- being generated -- if -- an instant -- a shutdown -- starting -- after that -- a film configuration -- stability -- maintaining -- having -- having excelled -- a shutdown -- effectiveness -- obtaining -- having had . On the other hand, what has the larger highest attainment temperature than (the melting point of +20 degrees C of polyethylene) requires time amount, after melting of polyethylene starts before resistance of porous membrane increases greatly, and membranous temperature can be interpreted as becoming larger than (the melting point of +20 degrees C of polyethylene) according to the current which flows in the meantime. When such porous membrane was included in a cell as a separator, initiation of a shutdown when an external short circuit arises could not maintain delay and a film configuration to stability greatly as compared with it at the time of using the film said whose highest attainment temperature is the following (melting point of +20 degrees C of polyethylene), and the outstanding shutdown effectiveness was not acquired. Moreover, before unlike the above the temperature of porous membrane continued rising after energization initiation

and the highest attainment temperature was shown, some which polypropylene fuses and generate a pinhole were. In addition, by the approach of supplying to the conventional dryer, the relation between temperature and an impedance was only seen. On the other hand, above, by the approach of this invention a publication, the phenomenon which cannot be predicted only by passing a minute current which measures an impedance in which a hole opens on the film can also be checked, and this just becomes important for the safety of a cell.

[0011] Moreover, the manufacture approach of the 1st porous membrane of this invention is made to porosity-ize by extending one shaft of filmy materials which mixed and become so that the rate of combination of said polyethylene may become 12 % of the weight or more about polyethylene with larger crystallinity than 60%, and polypropylene with larger crystallinity than 70%. According to this manufacture approach, if the porous membrane of this invention which has said temperature characteristic, i.e., melting of polyethylene, starts, the porous membrane to which the electric resistance increases to extent which can intercept a current immediately can be manufactured rationally.

[0012] Moreover, the manufacture approach of the 2nd porous membrane of this invention is made to porosity-ize by extending one shaft of filmy materials of a laminated structure with which the laminating of the 1st filmy material which comes to mix polyethylene with larger crystallinity than 60% and polypropylene



with larger crystallinity than 70%, and the 2nd filmy material which consists of polypropylene was carried out by turns, and it \*\*\*\*\*ed the rate of combination of the polyethylene per whole to 12% of the weight or more. While being able to manufacture rationally the porous membrane of this invention which has said temperature characteristic like said 1st manufacture approach according to this manufacture approach, the porous membrane obtained becomes a laminated structure containing the porous membrane of polypropylene, and the porous membrane by which a film configuration is maintained more by stability at the time of polyethylene melting can be obtained.

[0013] Moreover, the lithium ion rechargeable battery of this invention is constituted on both sides of what infiltrated the electrolytic solution into the porous membrane of this invention which has said temperature characteristic in inter-electrode [ of a pair ]. . By having made it such a configuration, even if it carries out an external short circuit, neither ignition nor short-circuit takes place, but is possible for the lithium ion rechargeable battery which operates stably.

[0014]

[Embodiment of the Invention] Although the porous membrane of this invention does not have the above mentioned temperature characteristic and especially the manufacture approach is not limited, there are no worries about environmental pollution in below, and a process (activity) explains an example of

the easy manufacture approach. In the approach of making it porosity-ize by this acquiring the process of the porous membrane currently performed from the former in this kind of field, i.e., the filmy material of the mixture (alloy) of polyethylene and polypropylene, and extending this filmy material It is an approach [ what / has the larger degree of crystallinity as polyethylene than 60% / (preferably 70% or more of thing) ] using what has the larger degree of crystallinity as polypropylene than 70% (preferably 80% or more of thing). In addition, generally 50 - 70% of polypropylene is conventionally used [ crystallinity ] for 40 - 60% of polyethylene, and crystallinity. Said degree of crystallinity is the value measured with the differential scanning calorimeter (DSC).

[0015] Although the reason used as what has the temperature characteristic which the porous membrane obtained by this process described above is not clear, this invention person has guessed as follows. Namely, even if it extends on the same conditions, the ingredient with high degree of crystallinity is easy to be extended. When the filmy material of polypropylene with larger polyethylene and crystallinity with larger crystallinity than 60% than 70% is extended, Rather than the case where the filmy material of 50 - 70% of polypropylene is extended, the both sides of polyethylene and polypropylene will be greatly extended [ 40 - 60% of polyethylene, and crystallinity ] for the conventional crystallinity

(polyethylene is extended especially greatly.). . Therefore, as shown in drawing 2 (a), polyethylene section 10a of the configuration extended flat will be surrounded by polypropylene section 10b by the porous membrane from which the polyethylene and crystallinity with larger crystallinity of this invention than 60% extend the filmy material of larger polypropylene than 70%, and are obtained. On the other hand, as shown in drawing 2 (b), globular form polyethylene section 10a will be substantially surrounded by polypropylene section 10b by the porous membrane from which 40 - 60% of polyethylene and crystallinity extend the filmy material of 50 - 70% of polypropylene, and the conventional crystallinity is obtained. In addition, the hole is formed in the both sides of polyethylene section 10a and polypropylene 10b although the hole is omitted by a diagram. Although a current will not flow to polyethylene section 10a, but a current will flow so that polypropylene section 10b may be sewn when polyethylene fuses by the temperature rise and the hole of polyethylene section 10a is closed also in any of the porous membrane of these both sides By the porous membrane of this invention of drawing 2 (a), the current path of a current 11 of flowing polypropylene section 10b is long, and the current path of a current 12 of flowing polypropylene section 10b becomes short by the conventional porous membrane of drawing 2 (b). Therefore, it will fall in the range in which resistance of the whole film increases greatly when polyethylene fused in the

porous membrane of this invention of drawing 2 (a) and the hole of polyethylene section 10a was closed, a current screening effect (the shutdown effectiveness) is acquired, membranous temperature once rises, and a maximum temperature does not exceed (the melting point of +20 degrees C of polyethylene). On the other hand, even if polyethylene fuses and the hole of polyethylene section 10a is closed by the conventional porous membrane of drawing 2 (b) In order for the current path length before the hole of polyethylene section 10a is closed (condition that a current flows through the hole in both polyethylene section 10a and polypropylene section 10b) to hardly change, When the polyethylene which the increment in resistance of the whole film in this time was small, and was fused after this closes the hole of polypropylene 10b It will fall, after going up to the temperature to which resistance of the whole film increases greatly, and a current screening effect (the shutdown effectiveness) is acquired, consequently membranous temperature exceeds (the melting point of +20 degrees C of polyethylene).

[0016] In the above, the shape-ization of film (film-izing) of the mixture (alloy) of polyethylene and polypropylene is performed by well-known approaches, such as for example, a T-die extrusion method and a tubular film process. moreover, as an approach of extending the filmy material of the alloy of polyethylene and polypropylene How to extend to 1 shaft orientations by approaches, such as roll

extension and tenter extension, (the 1st approach), How to extend again in a high temperature field in the same extension direction as the extension direction of this extension, after extending one shaft in a field whenever [ low-temperature ] (the 2nd approach), How to change the extension direction with the extension direction of this extension, and extend again in a high temperature field, after extending one shaft in a field whenever [ low-temperature ] (the 3rd approach), After extending one shaft in a field whenever [ low-temperature ], it extends again in a high temperature field in the same extension direction as the extension direction of this extension, and the method (the 4th approach) of changing the extension direction to this extension further, and performing third-time degree extension etc. is adopted. When the melting point of polyethylene is made into  $T_{mb}^{\circ}\text{C}$  by the 1st method of performing one extension, it is desirable to carry out in the temperature field of  $-20^{\circ}\text{C} - (T_{mb}-2)^{\circ}\text{C}$  \*\*. Moreover, when the melting point of polyethylene is made into  $T_{mb}^{\circ}\text{C}$ , it is [ whenever / low-temperature / in the 2nd which performs two extensions or more - the 4th approach ] desirable [ a field and a high temperature field ] that a field is a temperature field of  $-20^{\circ}\text{C} - (T_{mb}-30)^{\circ}\text{C}$  \*\* whenever [ low-temperature ], and a high temperature field is a temperature field of  $^{\circ}\text{C} - (T_{mb}-2)^{\circ}\text{C}$  \*\*. This is because the desirable aperture (0.005-1 micrometer) which it is extended efficiently, and

expansion-ization of an aperture is moreover fully made, and mentions performing each extension in these temperature fields and a filmy material later, and the porous membrane which has a void content (20 - 80%) can be obtained with sufficient repeatability. Moreover, when it extends by the 4th approach, in the point of making a hole existing uniformly in expansion-izing and the film of an aperture, a more desirable result is brought about rather than the 1st - the 3rd approach. Generally the draw magnification of the filmy material at the time of performing extension by these extension approaches, i.e., the draw magnification expressed with the following formula (several 1), is 20 - 300% preferably 5 to 600%. The inside of a formula (several 1), and L0 The die length of the filmy material before extension, and L1 It is the die length of the final filmy material after extension.

[0017]

[Equation 1]

[0018] moreover, the 2nd - the 4th approach of consisting of an extension process of multiple times also in the 1st approach of consisting of 1 time of an extension process -- also setting -- the extension rate in each process -- general

-- 10 - 5000% / min -- they are 100 - 1000% / min preferably.

[0019] Although the above explained the porous membrane which consists of one layer of porous membrane of the alloy of polyethylene and polypropylene. Also in the porous membrane of the type which carried out the laminating of the polyethylene proposed from the former, the porous membrane (alloy layer) of the alloy of polypropylene, and the porous membrane (polypropylene layer) of polypropylene. In case the alloy layer of polyethylene and polypropylene is obtained, it is made at the porous membrane which has the heated temperature characteristic of this invention by using polyethylene with larger crystallinity than 60%, and polypropylene with larger crystallinity than 70%. That is, the laminating of polyethylene with larger crystallinity than 60%, the filmy material of the alloy of polypropylene with larger crystallinity than 70%, and the filmy material of polypropylene is carried out, and this is extended and porosity-ized by the same extension approach as the above. Laminated structures here may be any of the two-layer structure of an alloy layer and a polypropylene layer, 3 layer structures which put the polypropylene layer on both the principal planes of an alloy layer, 3 layer structures which put the alloy layer on both the principal planes of a polypropylene layer, and the multilayer structure which carried out the laminating so that a number of layers total by turns [ of an alloy layer and a polypropylene layer ] might become four or more layers.

[0020] Moreover, even if it is the case where the porous membrane of the type which carried out the laminating of polyethylene, the porous membrane (alloy layer) of the alloy of polypropylene, and the porous membrane (polypropylene layer) of polypropylene is obtained even if it is the case where the porous membrane which consists of one layer of porous membrane of the alloy of polyethylene and polypropylene is obtained, before extending a filmy material, annealing can be performed to a filmy material. This annealing serves to raise a void content at the time of porosity-izing. As for this annealing, it is desirable to carry out in the temperature field of  $T_{mb-30}$  -  $T_{mb-2}$ , and it is performed for several seconds to about several hours.

[0021] When manufacturing the porous membrane of this invention by the above manufacture approach, it is checked by experiment that the rate of combination of the polyethylene to the whole film must be carried out to 12% of the weight or more. Probably, when not filling the rate of combination of polyethylene to 12% of the weight, the abundance of this of the polyethylene section which exists in the configuration extended flat in the film decreases too much, and it is considered to be because for huge-ization to no longer be made fully in a current path. Moreover, when the rate of combination of the polyethylene to the whole film exceeds 90 % of the weight, when polyethylene fuses, there is a case where it becomes impossible to maintain a film configuration, and, as for the upper limit



of the rate of combination of the polyethylene to the whole film, it is desirable to carry out to 90% of the weight.

[0022] Generally 0.005-1 micrometer of apertures of the porous membrane of this invention is 0.01-0.5 micrometers preferably. Generally a void content is 30 - 70% preferably 20 to 80%. Moreover, especially the class of polyethylene which constitutes the porous membrane of this invention is not limited, and can use various polyethylene, such as polyethylene of a low consistency, semi-gross density, or high density, and straight chain-like polyethylene. Moreover, although especially the class of polypropylene is not necessarily limited, either, in order to obtain a high void content, it is desirable that an isotactic index uses 95% or more of isotactic polypropylene preferably 90% or more.

[0023] Of course, the porous membrane of this invention can be used also as a separator of a lithium (ion) primary cell or other type cells not only in the separator of a lithium rechargeable battery.

[0024]

[Example]

(Example 1) After preparing polypropylene of 80% of crystallinity and mixing these with polyethylene of 70% of crystallinity at a rate of a mixing ratio (polyethylene: polypropylene) 6:4, it film-ized, and heat was applied (at 115 degrees C), 1 shaft extension of 160% of draw magnification was performed,

and thickness produced the porous membrane 0.04 micrometers and whose void content 25 micrometers and an average aperture are 45%. And the electrolytic solution (LiBF<sub>4</sub> mixed solution of melting propylene carbonate and DME (dimethoxyethane)) was sunk into this porous membrane, and both principal planes were inserted with the electrode made from stainless steel. And both this principal plane carried in the evaluation testing machine which showed the porous membrane pinched with the electrode to said drawing 1 , and impressed sinusoidal alternating voltage with a frequency of 100kHz by actual-value 35V. The rate of a temperature rise at this time (average for 2 - 5 seconds after energization initiation) was 20 degrees C/second. Drawing 3 was drawing having shown the temperature-change property of the porous membrane after sinusoidal alternating-voltage impression initiation, and after it reached the highest attainment temperature and about 5.5 minutes passed in about 2 minutes after electrical-potential-difference impression initiation, temperature fell. The highest attainment temperature was 125 degrees C, and this was 145 degrees C or less which is (the melting point of +20 degrees C of polyethylene (125 degrees C)). And this porous membrane was included in the lithium ion rechargeable battery, it changed into the overcharge condition (it charges by after [ a full charge ] 1C for 1 hour, and is 200% of charge condition), and the external short-circuit test was performed. A lithium ion rechargeable

battery here it is  $\text{LiCoO}_2$  as an active material to aluminum foil. Apply the carbon as a conductive auxiliary, and the mixture of N-methyl pyrrolidone (NMP), and it dries. Between the negative-electrode material which applied the graphite as an active material, and the mixture of NMP to the positive-electrode material and electrolytic copper foil which were obtained, and was obtained by drying it is  $\text{LiPF}_6$  in 1l. of solutions which carried out equivalent (volume ratio 1:1) mixing of ethylene carbonate (EC) and the DMC (dimethyl carbonate) at said porous membrane. Two or more layered products which come to insert that into which the electrolytic solution which dissolved one mol was infiltrated are twisted around the surroundings of a center pin in piles. It is the size AA battery which holds this winding object in a negative-electrode can, and it comes to close with a positive-electrode lid (the relief valve is prepared in the negative-electrode can.). . As a result of the external short-circuit test, short-circuit or ignition did not take place at all, but the cell operated to stability, and cell condensed mercury temperature was also 100 degrees C or less. In addition, [C] of said 1C is a unit showing the magnitude of the charge and discharge current of a cell, and 1C shows the current value which changes a cell into a full charge condition (from a full charge condition to a full discharge condition) for 1 hour after a full discharge condition (for example, by the cell of 750mAh,  $750 \times 2 = 1500\text{mA}$  and 0.5C are set [ 1C ] to  $750 / 2 = 350\text{mA}$  by 750mA and 2C).

[0025] (Example 1 of a comparison) Porous membrane was obtained like said example 1 except having used polyethylene of 50% of crystallinity, and polypropylene of 60% of crystallinity. And the trial same about this porous membrane as said example 1 was performed. Drawing 4 is drawing having shown the temperature-change property of the porous membrane after the sinusoidal alternating-voltage impression initiation at this time, and was attained to 150 degrees C in about 20 seconds after electrical-potential-difference impression initiation. Although it could expect that the highest attainment temperature was still higher, since porous membrane fused and between the positive-electrode-negative electrode short-circuited when electrical-potential-difference impression was continued and it went, the safety device of a power source worked, energization stopped, and the measurement beyond this became impossible. And when this porous membrane was included in the cell like said example 1 and the external short-circuit test after overcharge was performed, cell condensed mercury temperature rose [ two pieces ] at 120 degrees C or more among ten cells.

[0026] (Example 2) After preparing polyethylene of 70% of crystallinity, and polypropylene of 80% of crystallinity and mixing these at a rate of a mixing ratio (polyethylene: polypropylene) 5:5, (film-izing) and the 1st filmy material (film) was obtained. [ the shape of film ] Moreover, the 2nd filmy material (film) which

consists of a polypropylene simple substance was produced independently. And the 2nd filmy material was put on both the principal planes of the 1st filmy material (film), respectively, heat was applied for this laminated material (at 115 degrees C), 1 shaft extension of 160% of draw magnification was performed, and the laminating porous membrane whose thickness is 25 micrometers was produced. The ratio of the thickness of three layers was 1:1:1 and the rate of combination of the polyethylene per whole film was 16.7 % of the weight. And the trial same about this laminating porous membrane as said example 1 was performed. Drawing 5 is drawing having shown the temperature-change property of the porous membrane after the sinusoidal alternating-voltage impression initiation at this time, and reached the highest attainment temperature in about 11 minutes after electrical-potential-difference impression initiation. The highest attainment temperature was 127 degrees C, and this was 145 degrees C or less which is (the melting point of +20 degrees C of polyethylene (125 degrees C)). Then, when this porous membrane was included in the lithium ion rechargeable battery like said example 1 and the external short-circuit test was performed, short-circuit or ignition did not take place at all, but operated to stability, and cell condensed mercury temperature was also 100 degrees C or less.

[0027] (Example 2 of a comparison) As a raw material of the 1st filmy material

(film), crystallinity obtained the laminating porous membrane of the laminated structure of 3 layer structures like said example 2, except that crystallinity used 60% of polypropylene, 50% of polyethylene, and. And the trial same about this porous membrane as said example 1 was performed. Drawing 6 is drawing having shown the temperature-change property of the porous membrane after the sinusoidal alternating-voltage impression initiation at this time, the highest attainment temperature is 157 degrees C, and this became higher than 145 degrees C which is (the melting point of +20 degrees C of polyethylene (125 degrees C)). When this porous membrane was included in the lithium ion rechargeable battery and the external short-circuit test was performed like said example 1, cell condensed mercury temperature rose [ two pieces ] at 120 degrees C or more among ten cells.

[0028] (Example 3 of a comparison) the laminating porous membrane of the laminated structure of 3 layer structures was obtained like said example 2 except having set the ratio of the thickness of three layers to 2:1:2 (the 1st filmy material of middle -- porosity -- the thickness of the layer which were-izing [ the layer ] and was obtained -- small -- the 2nd filmy material of both \*\* -- porosity -- the thickness of the layer which were-izing [ the layer ] and was obtained -- greatly), and having carried out content of the polyethylene per whole film to 10% of the weight. Drawing 7 was drawing having shown the temperature-change property

of the porous membrane after the sinusoidal alternating-voltage impression initiation at this time, and the highest attainment temperature was 160 degrees C, and was higher than 145 degrees C which is (the melting point of +20 degrees C of polyethylene (125 degrees C)). Then, when this porous membrane was included in the lithium ion rechargeable battery and the external short-circuit test was performed like said example 1, cell condensed mercury temperature rose [ two pieces ] at 120 degrees C or more among ten cells.

[0029]

[Effect of the Invention] As mentioned above, according to this invention, it is the porous membrane which consists of polyethylene and polypropylene, and when it is used as a separator for cells, the porous membrane [ shut / to extent which can intercept a current / an instant / porous membrane / quantity-izes / resistance-/ and ] can be offered after the outstanding current screening effect (the shutdown effectiveness), i.e., melting of polyethylene. Moreover, the manufacture approach of porous membrane that the porous membrane of this this invention can be manufactured simply and rationally can be offered. Moreover, even if it carries out an external short circuit, neither ignition nor short-circuit takes place, but can offer the lithium ion rechargeable battery which operates stably.

## DESCRIPTION OF DRAWINGS

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### [Brief Description of the Drawings]

[Drawing 1] The temperature characteristic of porous membrane is the side elevation having shown the outline configuration of the evaluation testing machine to evaluate.

[Drawing 2] It is the cross-section perspective view having shown typically the membrane structure of the porous membrane of this invention, conventional polyethylene, and the alloy of polypropylene.

[Drawing 3] It is drawing having shown the temperature change of the porous membrane after sinusoidal alternating-voltage impression initiation of the porous membrane by the example 1.

[Drawing 4] It is drawing having shown the temperature change of the porous membrane after sinusoidal alternating-voltage impression initiation of the porous membrane by the example 1 of a comparison.

[Drawing 5] It is drawing having shown the temperature change of the porous membrane after sinusoidal alternating-voltage impression initiation of the porous membrane by the example 2.

[Drawing 6] It is drawing having shown the temperature change of the porous



membrane after sinusoidal alternating-voltage impression initiation of the porous membrane by the example 2 of a comparison.

[Drawing 7] It is drawing having shown the temperature change of the porous membrane after sinusoidal alternating-voltage impression initiation of the porous membrane by the example 3 of a comparison.

[Description of Notations]

1 Electrode

2 Electrode Which Served as Installation Base of Porous Membrane

3 Clip for Fixing Porous Membrane to Top Face of Electrode

4a Temperature sensor

4 Thermometer Which Outputs Temperature Detected with Temperature Sensor

5 AC Power Supply

10 Porous Membrane into which Electrolytic Solution Sank

10a Polyethylene section

10b Polypropylene section

11 12 Current